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(54) Iron-Copper Separation by Reduction Leaching

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T I T L E

IRON-COPPER SEPARATION BY REDUCTION LEACHING

I N V E N T O R S

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ABSTRACT OF THE DISCLOSURE

Iron-copper separation from sulfide minerals, concentrates, tailings or partial calcines containing these metals, has been achieved by leaching in acid sulphate solutions under reducing conditions to convert all of the unoxidized sulfur to chalcocite (Cu_2S) solids and to bring all of the iron into solution. It has been found that this reduction leach will proceed if there is present at least two moles of copper for each mole of sulfide and elemental sulfur, and a reducing agent able to complete all reduction reactions that yield chalcocite. Metallic copper powder has been found an adequate reducing agent and is able to supply any Cu needed to form Cu_2S . Iron powder or hydrogen gas under pressure are also operative reducing agents. This reduction leach is operative also on calcines from which sulfur has been volatilized, in which case a metallic copper concentrate is formed. Various flowsheets incorporating this reduction leach are described. This reduction leaching avoids H_2S evolution.

FIELD OF THE INVENTION

This invention is concerned with a hydrometallurgical process for treating materials comprising sulfides of copper and iron, and calcines thereof. A specific reduction leach has been found very effective for removing iron and rendering the copper very suitable for recovery, while avoiding H_2S emissions. If desired an initial roast step can be used to lower or remove the sulphur content in the feed (followed by the reduction leach).

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BACKGROUND AND PRIOR ART

The important sulphide minerals in most copper concentrates are chalcopyrite ($CuFeS_2$), bornite (Cu_5FeS_4), and pyrite (FeS_2). Every process for recovering copper from these concentrates involves a copper-iron separation, and the nature of the iron-containing component largely determines the extent of copper losses in the process, and the ease of recovery of valuable by-products (mainly silver and gold). In copper smelting, the iron component is a silicate slag containing about 40% Fe and up to 1% Cu.

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Precious metals and most other valuable minor metals follow the copper through the process and are recovered when the copper is refined. Because there is an incentive to eliminate atmospheric emissions of SO_2 associated with copper smelting, a variety of hydrometallurgical processes have been promoted in recent years for treating these same copper concentrates. Some of these hydrometallurgical processes have led to emissions of H_2S .

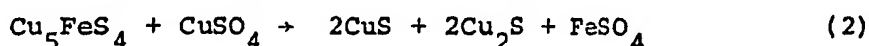
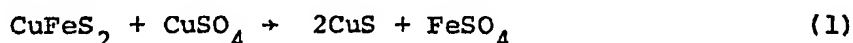
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When copper concentrates are leached directly, it is necessary to resolve the problem of the copper-iron separation. Typically, iron is left in leach residues if leaching is done in oxidizing ammoniacal solutions, or in weak oxidizing acid-sulphate solutions, and such high iron residues retain



precious metals and other minor values as dilute constituents, difficult to recover. In chloride systems, both iron and copper are dissolved in the leach, and the iron-copper separation must be solved in a later step. Direct leaching of iron only, leaving copper, precious metals, and minor values free of iron (as in smelting) can be accomplished only in a leach conducted under neutral or reducing conditions.

Historically, the first process for separating iron in such a reverse leach is due to McGauley et al United States Patent 2,568,963 (1951) (1) who found that iron could be leached from copper concentrates by copper sulphate solutions. The essential chemical reactions appeared to be:

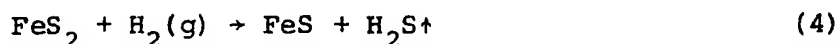
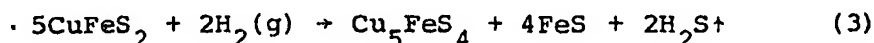


This is a neutral leach with substantial copper content in solution but no reducing agent. There is no evidence in this McGauley et al reference that pyrite (FeS_2) was decomposed, and extraction of iron was never very high, in spite of high temperatures ($180\text{--}200^\circ\text{C}$) and long residence times (4-12 hrs). In fact the process is regarded now as relatively impractical as a treatment of raw copper concentrates because the reaction is too slow. A variant of this reaction is included in the comprehensive S-C (Sherritt-Cominco) process (G.M. Swinkels and R.M.G.S. Berezowski, C.I.M. Bulletin, Feb. 1978, pp. 105-121) as a unit operation that extracts iron from material that has already been subject to an earlier and incomplete iron removal step and in which most of the remaining iron is in the form of bornite. Conditions of 156°C for 4 hours increased the iron extraction from 75% (from previous steps) to 91% overall, an increment of 16% of the total iron in the original concentrates, and an extraction of 64% of the iron exposed to this treatment.

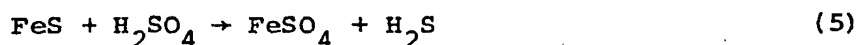
Final composition of copper concentrates after this treatment was 4% Fe and about 53% Cu.

Another leaching process that was found to leach iron selectively from copper concentrates utilized a galvanic reaction between copper powder and the sulphide minerals in sulphuric acid, to yield ferrous sulphate solutions and hydrogen sulphide gas (D.R. McKay and G.M. Swinkels, Canadian Patent No. 953935, Sept. 3, 1974; U.S. Patent 3,891,522 June 24, 1975. J.B. Hiskey and M.E. Wadsworth, Chapter 29 of Solution Mining Symposium (Aplan, McKinney, E. Pernicelle, editors) S.M.E. (A.I.M.E.) 1974) as well as solid residues with much improved copper-iron ratios. The reaction took place readily at atmospheric pressure and temperatures between ambient and about 90°C, with residence times of about 2 or 3 hours required at the higher temperatures for maximum obtainable conversions. However, while the reaction proceeds easily, it fails to go to completion, and iron extractions in excess of 80% are difficult to obtain at acid strengths that permit near neutralization. It is considered possible, in principle, to use a variety of metallic reducing agents or even cathodic reduction in reactions that dissolve iron and generate hydrogen sulphide from sulphide minerals. However, only the use of copper is really practical when treatment of conventional copper concentrates is contemplated. It would be desirable to avoid the H₂S emissions common to these processes.

In a variation of the S-C process, G.M. Swinkels, R.A. Furber, E.F.G. Milner, R.M.G.S. Berezowski and C.R. Kirby, U.S. Patent 3,964,901 (1976), have chosen to decompose the copper-iron minerals in copper concentrates by means of a dry thermal pretreatment at about 700°C that removes approximately 1/4 of the sulphur as H₂S. The effective stoichiometry of this reaction can be expressed by the equations:

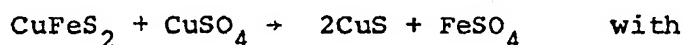


The intention is that all copper concentrates are converted into a mixture of bornite (Cu_5FeS_4) and pyrrhotite (FeS). The pyrrhotite is readily soluble in weak sulphuric acid, with elimination of H_2S , i.e.



It is an unfortunate characteristic of the thermal pre-treatment that at $\sim 700^\circ\text{C}$, the treatment temperature, the $\text{H}_2/\text{H}_2\text{S}$ ratio required for conversion of chalcopyrite is rather high, and the composition range (variation) of the chalcopyrite phase is so large that, on cooling, some of this phase reforms. Thus, the thermally treated concentrates are not completely free of chalcopyrite (CuFeS_2), as indicated by equation (3). The consequence is that acid leaching of the product according to equation (5) actually removes only 75% of the iron, leaving a residue that is mainly bornite (Cu_5FeS_4) but containing some residual chalcopyrite. A variation of the McGauley et al process decomposed the bornite and raised iron extractions to 91%. Unextracted iron appeared to be mainly in the form of chalcopyrite.

United States Patent 3,816,105 June 11, 1974,
D.R. McKay et al describes an activation leach of copper-iron sulfides with a sulfuric acid solution containing copper ions under non-oxidizing conditions. The main reaction for chalcopyrite is said to be equation (1)



the CuS being insoluble. Some ferric ions are usually present, leading to solubilization of some sulfide Cu as CuSO_4 .

Preferably the activation leach was carried out under pressure

at about 120-160°C. The amount of sulfuric acid used, e.g. in the recycled acid solution, for this leach was 5-35 g H_2SO_4/L . From the examples it is evident that considerable iron was left in the leached solids. It would be desirable to leach substantially all of the iron without solubilizing significant amounts of copper in one step (and thus achieve a good Cu-Fe separation).

United States Patent 3,891,522 June 24, 1975,
D.R. McKay et al is similar to 3,816,105 except that some
10 metallic copper is introduced to act as a reducing agent on the copper-iron sulfides and generally higher acid concentrations and lower temperatures are utilized in the activation leach i.e. 15-250 g H_2SO_4/L and about 60-95°C. The principal reaction with chalcopyrite is



Some H_2S is evolved and it would be desirable to avoid this.

There is evidence that the "activation leach" as carried out in these latter two patents of McKay et al
20 were unable to decompose pyrite (FeS_2) and pyrrhotite (FeS) as well as chalcopyrite and bornite. It would be desirable to have a leach which would decompose all iron sulfides and yet precipitate cuprous sulfide.

United States Patent 3,957,602 May 18, 1976
R.K. Johnson et al describes a leach of chalcopyrite with copper sulfate solution under conditions which form primarily digenite (Cu_9S_5), a soluble iron sulfate, and sulfuric acid. The conversions of Cu to digenite were within about 74-80% and a secondary leach was usually carried out.

30 In United States Patent 3,985,555 M.B. Shirts et al chalcopyrite is decomposed by reaction with acid in aqueous solution in the presence of a metallic reductant at 100°C

or less. The metallic reductant may be copper powder. The process carried out invariably gave rise to H_2S emission.

All of the above processes are unsatisfactory in one or more of the following characteristics:

- 1) Inadequate iron extractions
- 2) Difficult or costly furnace pretreatment
- 3) Reaction too slow
- 4) Evolution of H_2S , a dangerous gas.

Only the S-C process is believed to fall within acceptable economic constraints for a copper recovery process that competes with smelting, and this S-C process achieves the copper-iron separation by three steps in series, namely:

- (i) thermal pretreatment with hydrogen
- (ii) acid leaching to remove pyrrhotite, and
- (iii) an "activation" leach corresponding to the McGauley et al process step.

A process that can achieve the same results with fewer steps would be of interest if it did not introduce any difficult consequences in the rest of the flowsheet.

SUMMARY OF THE INVENTION

It has now been found that a reduction leach process at within 100° - $200^{\circ}C$ can be controlled to solubilize substantially all of the iron while allowing high copper recoveries. Emissions of H_2S can be avoided either by the provision of excess copper, e.g. as $CuSO_4$ and/or Cu metal, to form Cu_2S exclusively, or by partial or complete calcination to eliminate enough sulphur so that any remaining sulphur can be converted only to Cu_2S .

This invention is directed to a method of removing iron and recovering copper from minerals, concentrates, tailings or partial calcines comprising these metals at

least partly in sulfide form, or from complete calcines thereof in non-sulfide form, comprising:

- (a) reduction leaching said minerals, concentrates, tailings, partial calcines or complete calcines with an aqueous solution containing sulfuric acid in amounts of the order of about 2 to about 20 g H_2SO_4 /L, at temperatures within about 100°C to about 200°C , under sufficient pressure to avoid loss of water or gas, and while maintaining reducing conditions; said acid concentration and reducing conditions being sufficient to convert substantially all iron present to soluble ferrous salts;
- (b) in the case of sulfides being leached, providing that a sufficient excess of copper is present to react with all sulfur to form insoluble chalcocite Cu_2S and thereby avoid H_2S emission;
- (c) separating the leach liquor containing dissolved iron sulphate from solids; and
- (d) recovering solids containing copper substantially entirely in at least one of the forms Cu_2S and metallic copper.

The method may include the subsequent steps of

- (e) subjecting recovered solids which contain Cu_2S to a second leach step comprising an oxidizing leach;
- (f) separating this second leach liquor from unleached solids; and
- (g) recovering copper from this second leach solution.

The method may include initial steps wherein prior to the reduction leach (a) the feed material is subjected to a partial roast step at about $700 - 900^\circ\text{C}$ to remove gases containing sulfur dioxide and the partial calcine fed to reduction leach (a). Alternatively the feed material initially is dead-roasted at about 700°C

to remove sulfur and the resulting calcine then reduction leached, the solid residue being recovered as a metallic copper concentrate.

DESCRIPTION OF THE DRAWINGS

Figure 1 is a flowsheet diagram of one option according to the invention where copper concentrates without roasting are subject to the reduction leach in the presence of excess copper (powder), followed by separation, recovery and recycle steps.

10 Figure 2 is a flowsheet where an optional partial roast has been carried out initially on the concentrate followed by the reduction leach and other preferred separation, recovery, and recycle steps.

Figure 3A is a flowsheet of a further optional process according to the invention where an initial dead roast is carried out followed by the reduction leach for iron removal, yielding a metallic copper concentrate.

20 Figure 3B is similar to Figure 3A except that a strong acid leach is included after the reduction leach to assure substantially complete iron separation.

DETAILED DESCRIPTION AND PREFERRED EMBODIMENTS

The material fed to the reduction leach can be any ore, concentrate, tailing or partial calcine of any of these, comprising sulfides of copper and of iron. These materials usually contain pyrites, chalcopyrites, bornite, covellite or pyrrhotite as well as impurities including siliceous minerals and other metals. In most cases the feed material will have been subjected to some form of concentration to remove non-sulfides.

30 In one aspect of the invention, the sulfide feed material can be subject to an initial roast step to volatilize sulfur (as SO_2 which may be used to make sulfuric acid for the

reduction leach and any secondary leach). The roast can be controlled to remove only part of the sulfur (in which case the recycling load of copper to form Cu_2S in Figures 1 and 2 can be reduced) or to remove all of the sulfur (in which case the reduction leach will form a metallic copper concentrate very suitable for copper recovery - Fig. 3). The feed to the reduction leach thus can be a partial or complete calcine.

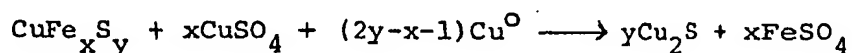
The reduction leach does not require high acid concentrations: amounts of the order of about 2 to about 20g $\text{H}_2\text{SO}_4/\text{L}$ are sufficient. Leach temperatures may vary within about 100°C-200°C under the appropriate pressure. The reducing conditions may be provided by a selected reducing agent from the group: metallic copper, metallic iron powder, hydrogen-containing reducing gases and organic reducing agents. The combination of acid concentration and reducing conditions should be controlled to be sufficient to convert substantially all iron present to soluble ferrous salts in the leachant. In the case of calcines, preferably the reducing agent is hydrogen or hydrogen-containing reducing gas.

During the reduction leaching a buffer may be present selected from ammonium sulfate, sodium sulfate, magnesium sulfate, and other equivalent buffers. The amount of such buffers may range most suitably from about 10 to about 100g/L measured as sulfate. Desirably, sufficient buffer is present to lower corrosion rates on stainless steel equipment and to improve subsequent steps, such as separating iron from ferrous sulfate solutions as jarosite.

Process Option I Sulfide Concentrates Only (Figure 1)

A. Reduction Leach

One preferred form of the reduction leach is represented by the equations:



where $\text{CuFe}_{x-y}\text{S}_y$ represents the mean composition of the copper concentrates, including minerals like chalcopyrite (CuFeS_2), pyrite (FeS_2), bornite (Cu_5FeS_4), and covellite (CuS). Metallic copper of impure grade, such as atomized scrap, cement copper, purification copper, and recycled hydrogen reduced copper is the preferred reducing agent.

10 The reduction leach preferably takes place at 140°C or higher, with no special atmosphere (except absence of oxygen) and leads typically to 95% iron extraction in $1\frac{1}{2}$ hours at 140°C for as-received copper concentrates and -230 mesh copper powder. The reaction is accelerated by higher temperatures, or by finer copper powder. It is exothermic enough to provide for at least 30°C of adiabatic temperature jump (for a reaction in which 70 g/L iron is leached). The reduction leach takes place at high pulp densities (typically 200-300 g/L concentrates, in addition to copper metal).

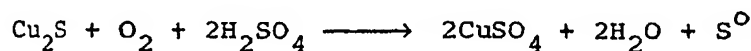
20 For chalcopyrite concentrates, the copper reagent burden is large - about 2 tons metal powder and one ton Cu as copper sulfate leach solution for each ton of copper in concentrates. This would be much lower for high bornite concentrates, because the copper reagent requirement for bornite is only 0.4 tons metal and 0.2 tons copper as copper sulfate, for each ton of copper contained as bornite.

Solutions from the reduction leach usually are destined for jarosite oxydrolisis, and so preferably should be low in copper (less than 3g/L). Solid leach residues should be low in iron (less than 1%) and are destined for copper recovery usually by oxygen pressure leaching.

B. Oxidizing Pressure Leach for Copper

3 The product of reduction leaching in this Option I, is chalcocite, Cu_2S , or djurleite, $\text{Cu}_{1.96}\text{S}$, which is generally of finer particle size than the original copper concentrates,

because of volume increases and spalling of particles in the reduction leach. The stoichiometry of the oxidizing pressure leach may be represented by:



Chalcocite leaches readily at 100°C and 100-200 psig oxygen pressure in agitated autoclaves. However, to obtain very high extractions (>99%), very long residence times may be necessary.

The flow diagram (Fig. 1) shows that extractions actually are controlled by recycling an appropriate fraction of sulfide residues to the leach. For example, if 99.75% extraction is necessary (100% of recycled copper and 99% of copper in the incoming concentrates), while only 97.5% of copper is extracted during the leach, then 90% of the sulfides recovered from residue treatment must be recycled to the leach (after silica and elemental sulfur removal).

Acid feed to the oxidizing leach normally comes from three sources:

- (a) Recycled acid from hydrogen reduction, carrying typically about 20 g/L Cu and 4 g/L Fe as well as about 120 g/L H_2SO_4 and 0.8 M. $(\text{NH}_4)_2\text{SO}_4$.
- (b) Weak acid from jarosite oxyhydrolysis, carrying typically 1 g/L Fe, < 3 g/L Cu, ~60 g/L H_2SO_4 , and 0.8 M. $(\text{NH}_4)_2\text{SO}_4$.
- (c) New H_2SO_4 , added as 96-100% H_2SO_4 with no significant impurities.

The combination of these solutions will lead to a weighted average feed to the oxidizing leach of 16 g/L Cu, 3.5 g/L Fe, 120 g/L H_2SO_4 and 0.8 M. $(\text{NH}_4)_2\text{SO}_4$. The target pregnant solution is about 80 g/L Cu, 4 g/L Fe, 20 g/L free H_2SO_4 , and 0.8 M. $(\text{NH}_4)_2\text{SO}_4$. This secondary leach is very similar to that of the S-C process and is assumed to require similar total residence times (~ 7.5 hrs.).

C. Purification

The pregnant solution from oxidizing leach B contains impurities such as Se, Te, As, Sb, and perhaps Bi. The first two of these elements, Se and Te, will precipitate quantitatively with copper during hydrogen reduction, and so must be removed. The preferred purification method is to displace these elements with copper powder destined for recycling to the reduction leach. This should lower Se from (typically) 1.2 mg/L to <.05 mg/L, a target necessary to keep Se in precipitated copper to <1 p.p.m. Purification will work satisfactorily to meet these specifications with about 30 g/L Cu at 140°C (the solution passing through a vertical leaf pressure filter to the hydrogen reduction autoclave). The copper contaminated with selenium and tellurium is returned to the reduction leach. Since less than 5% of the selenium and tellurium in chalcocite is leached (it mainly reports to elemental sulfur), that portion of selenium that does leach can be recycled without risk of solution build-up in the circuit.

D. Hydrogen Reduction

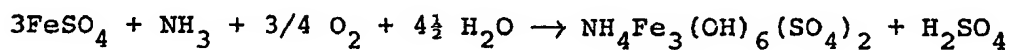
Hydrogen reduction precipitates copper and regenerates acid, i.e., $\text{H}_2 + \text{CuSO}_4 \rightarrow \text{Cu}^0 + \text{H}_2\text{SO}_4$. Hydrogen reduction in Figure 1, preferably is conducted at 140 to 180°C at 200-800 psig hydrogen pressure, and is state of art. Surfactants such as ammonium polyacrylate are normally added to avoid "plastering" of metal. Corrosion of high nickel stainless steels or titanium is inhibited by operating with a buffer (0.8 - 1.0 M. $(\text{NH}_4)_2\text{SO}_4$) and by restricting copper recovery to about 60 g/L (from 80 g/L in feed solution to ~ 20 g/L in discharge solution). The residual copper is a powerful corrosion inhibitor.

Normal hydrogen reduction practice involves "densification", i.e. leaving copper metal in the autoclave

(operated in batch cycles) as barren solution is discharged and new lots of pregnant solution are charged. Such practice would coarsen the copper to some degree - an undesirable feature for powder desired for purification or in the reduction leach. Therefore, hydrogen reduction practice would not be quite "normal" in that powder may be discharged continuously and classified, to isolate finer material for recycle and coarser material for melting and casting.

E. Oxydrolisis

Strong ferrous sulfate solutions can be converted to a hydrolyzed iron product (jarosite) and weak acid, according to the stoichiometry:



The S-C process performs this reaction on solutions containing 60-90 g/L Fe and 5-15 g/L free H_2SO_4 (no Cu). The indicated pilot plant results show that if the feed contains 57 g/L Fe and 15 g/L H_2SO_4 , the final solution will contain 5 g/L Fe and 50 g/L H_2SO_4 (as well as 2 g/L NH_3) after treatment at 190°C and a mean retention time of 45 minutes in a four-compartment continuous autoclave. The jarosite solids assayed 34% Fe, 2.6% NH_3 and 13% S. Our calculations indicate that in the presence of 0.8 - 1 M. excess $(\text{NH}_4)_2\text{SO}_4$ as a buffering agent, with a feed of 70 g/L Fe and 20 g/L free H_2SO_4 , the product solution should contain only ~1 g/L of Fe and 60 g/L free H_2SO_4 , given the same conditions of treatment. If Cu is <3 g/L, the resulting jarosite should contain <.02% Cu, which would permit possible conversion of jarosite to high grade iron ore by calcination with sulfur removal. Normally, however, the jarosite would be regarded as a discardable waste.

Residue Treatment and Precious Metals Recovery

Leach residues may be expected to contain precious metals as well as silicious minerals, elemental sulfur, and certain refractory minerals (i.e. arsenopyrite). The normal treatment may be (a) flotation, to reject silicious material, (b) elemental sulfur removal, by liquid sulfur filtration and/or dissolution in organic or aqueous (alkaline) sulfur solvents, and (c) splitting into a precious metals concentrate for shipment and a recycle sulfide concentrate (returned to the oxidizing leach for enhanced copper extraction). Since the fraction of the sulfide split off for recycle increases copper extraction and can be controlled, this split acts as a final guarantee that copper extractions can be enhanced and controlled without prolonged residence times in the oxidizing leach. The incompletely leached particles are given additional residence time by recycling, and additional reactivity by sulfur removal. The amount of unleached copper shipped with precious metals and so lost from the circuit may be consciously chosen by the plant manager, who thus determines ultimate recovery.

Summary of Process Option I

This option contains no pyrometallurgy and, therefore, no gas treatment demands for either noxious gas or dust abatement purposes. It is entirely hydrometallurgical and provides for high recovery of copper and elemental sulfur, as well as separation of elemental sulfur and a relatively pure iron compound (jarosite). Because sulfate is rejected in the jarosite, new sulfuric acid must be purchased, corresponding to about 1/3 of the sulfur produced by the process. All steps in the process are exothermic, although some are not sufficiently so to permit operation without additional thermal energy input.

Precious metals are recovered from the process as a P.M. concentrate suitable for shipment or special treatment.

A penalty of the option I process is that it requires a large circulating load of copper, because both copper powder and copper sulfate solution are reagents in the reduction leach. The consequence of this circulating load is that for chalcopyrite concentrates, the leaching plant is 4 times as large and the hydrogen reduction plant 3 times as large as if there were no circulating loads of CuSO_4 or Cu^0 . For high bornite concentrates, these values are substantially reduced.

Process Option II has been developed (see Figure 2) as a means of reducing the circulating load of copper powder and/or copper sulfate. However, option II contains some pyrometallurgy, with attendant gas and dust handling and sulfuric acid production.

Process Option II Partial Roast (Figure 2)

The reduction leach in option II converts all sulfide sulfur contained in the total feed to chalcocite (Cu_2S). To convert all the sulfur present as chalcopyrite (CuFeS_2) to chalcocite requires three units of copper for each unit of copper present in the mineral. This represents a large circulating load of copper, as seen in option I. However, part of this sulfur can be eliminated by roasting, and this will lower the circulating load of copper needed for the reduction leach. For typical chalcopyrite concentrates, the limit that can be roasted is 75% of the concentrates, as this reduces the circulating load of copper to zero. If there is more than 4 moles of copper per mole of sulfide sulfur in the feed to the reduction leach, excess copper will either leave the leach as dissolved copper sulfate, or it will be reduced

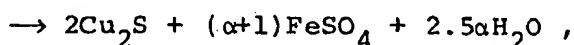
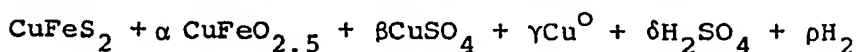
to metallic copper entrained in the chalcocite that is formed. For the purpose of this option, it is assumed that no metallic copper is desired in the reduction leach product, and that copper sulfate remaining in reduction leach liquor (ferrous sulfate solution) should be minimized (say less than 3 g/L copper contained). Option II contains the full range of calcine/concentrate ratios that leads to the formation of chalcocite (Cu_2S) in the reduction leach.

Operating Conditions in Process Option II (Figure 2)

10 A. Reduction Leach e.g. $140\text{--}180^\circ\text{C}$; 1-2 hr; 400 psig H_2

The reaction at 140°C was incomplete, especially with respect to iron extraction. Test results on a concentrate-calcine mixture indicated only 75% Fe extraction under standard conditions. If this can be increased to 95% by going to 180°C for a given feed material, this will solve the problem directly. Otherwise, a scavenger acid leach (to decompose unleached copper ferrite) will need to be added to the circuit (as shown in the flowsheet Figure 2). The reduction leach must take place under hydrogen pressure, even if metallic copper is incorporated as a reducing agent. The reason is that the calcines contain ferric iron, as well as copper oxide. Copper metal is not a reducing agent for copper oxide or dissolved copper. However, the flowsheet Figure 2 depicts some copper metal as a purifying agent for removal of selenium and tellurium, and this copper, as well as cement copper and powdered (atomized) scrap copper, can be added to the reduction leach, lowering the amount of concentrate that needs to be roasted.

The reduction leach in this option II has the following stoichiometry (assuming chalcopyrite concentrates):



Here $\alpha + \beta + \gamma = 3$; $\beta + \delta = \alpha + 1$; $\delta + \rho = 2.5 \alpha$.

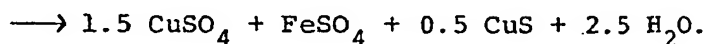
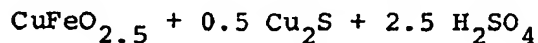
The limiting condition of maximum calcine utilization is for the case where $\alpha = 3$, $\beta = 0$, $\gamma = 0$, $\delta = 4$, and $\rho = 3.5$. The Option I stoichiometry occurs when $\alpha = 0$, $\beta = 1$, $\gamma = 2$, and δ and ρ are both 0. An intermediate stoichiometry occurs when $\alpha = 1$ (50% of concentrates roasted). In this case $\beta = 0$ to 2, $\gamma = 2$ to 0, $\delta = 2$ to 0, and $\rho = 0.5$ to 2.5. These ranges illustrate that metallic copper can substitute for some, but not all of the reducing agent when calcines are present.

0 Examples are shown only for conditions close to this intermediate situation.

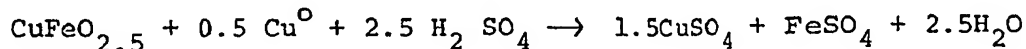
Note that it is considered possible to use organic reducing agents as a substitute for hydrogen; examples are: methanol (CH_3OH); formaldehyde (H_2CO); methyl formate ($\text{CH}_3\text{OH} \cdot \text{HCOOH}$); formic acid (HCOOH); oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$); sugars ($\text{C}_6\text{H}_{12}\text{O}_6$) or starches ($\text{C}_6\text{H}_{10}\text{O}_5$). Hydrazine (N_2H_4) is an established reducing agent much more reactive than hydrogen, but may be too expensive to consider. Use of still other reducing agents such as SO_2 may be feasible.

20 B. Scavenging Acid Leach (Fig. 2)

This leach will be necessary to decompose residual copper ferrites if modifications to the reduction leach fail to achieve adequate iron extractions. Optimum leach conditions have not been established, but may suitably be about 100°C in unpressurized equipment, with excess acid in terms of the stoichiometric requirement for the reaction:

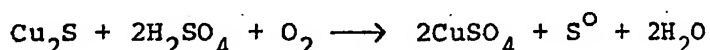


This scavenging leach may benefit from input of recycled copper powder, which would eliminate the leaching of Cu_2S , and improve reaction rate. The stoichiometry would be similar, i.e.



C. Oxidizing Leach (Fig. 2)

This leach is the same as in process option I (Fig. 1 B). The stoichiometry is written:



One set of preferred conditions is: 100°C ; 200 psig; $7\frac{1}{2}$ hr. mean residence time.

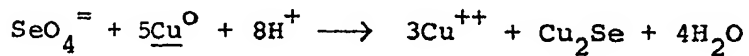
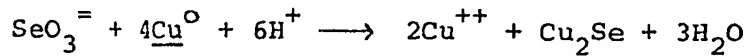
It is considered necessary for this leach to obtain copper extractions of greater than 99%, in order for the process to be competitive. Ultimate extractions can be raised by recycling some of the sulfide residues (after removal of elemental sulfur) to the leach. This also recycles precious metals contained in these residues. A portion of sulfide residues containing less than 1% of the copper in the feed suitably is transferred to a precious metals recovery system or shipped to a custom smelter for precious metal and residual copper recovery.

D. Purification (Fig. 2)

The pregnant solution from Fig. 2 C is expected to contain about 80 g/L copper, 4 g/L Fe, and 20 g/L free H_2SO_4 . Part of this is destined to return to the reduction leach A as a source of copper sulfate; however, the bulk of the pregnant solution is destined for copper recovery by hydrogen reduction, and for this purpose it must be purified of those impurities that will contaminate hydrogen-reduced copper powder.

The most important impurities of this kind are selenium and

tellurium. Purification of this type usually is by cementation on copper powder. Selenium and tellurium, being more noble than copper, are rapidly removed according to the following reactions:



Purification at 140°C was tested, and proved to remove selenium and tellurium in negligible residence times. More suitably, operative conditions may include boiling temperatures (100°C) in an agitated tank from which air is excluded, for residence times of about $\frac{1}{2}$ hr., if the cementation copper is present as -200 mesh material at 20 g/L pulp density (these latter conditions have not been confirmed). Selenium and tellurium content of purified solution desirably should be less than 0.06 mg/L. Selenium is hardly leached in the oxidizing leach C, the extraction being only 2-4%. Therefore, recycled selenium (and, presumably, tellurium) does not lead to impurity build-up in the circuit. The final deportment of these elements is to elemental sulfur.

E. Hydrogen Reduction (Fig. 2)

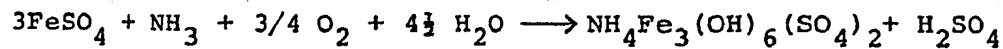
Hydrogen reduction is the chosen method of winning copper from purified pregnant solution, because (a) powdered copper is a required reagent for the reduction leach and for purification and (b) hydrogen reduced copper can, in principle at least, be made sufficiently pure for markets. The marketed material would need to be melted and cast.

For reasons of controlling product purity, it would be desirable to leave 10 to 20 g/L Cu in the return acid from hydrogen reduction. If the solution is "buffered" with 1 M. $(\text{NH}_4)_2\text{SO}_4$, the hydrogen reduction can be conducted at 140 to 160°C in about 2 hrs. at 400 psig H_2 pressure. The reaction is moderately exothermic.

Hydrogen reduction is regarded a state-of-art, but may require specially lined reactors to avoid corrosion, as well as selected additions of surfactants such as ammonium polyacrylates to avoid "plastering".

F. Oxydrolisis (Fig. 2)

Suitably ferrous sulfate solution containing at least 70 g/L Fe and less than 3 g/L Cu, with less than 20 g/L free H_2SO_4 and 1 M. ammonium sulfate is reacted at $\sim 200^\circ\text{C}$ with oxygen and ammonia. The reaction stoichiometry may be written:



This reaction also takes place as in the S-C process except that 1 M. $(\text{NH}_4)_2\text{SO}_4$ buffers the system, and the Fe content is slightly higher. A test comparison with the S-C process is as follows:

<u>Feed Stream</u>	<u>S-C Process</u>	<u>Reduction Leach Process</u>
Fe g/L	> 57	> 70
H_2SO_4 g/L	15	20
$(\text{NH}_4)_2\text{SO}_4$ g/L	-	132
Cu g/L	-	< 3
<u>Product Liquor</u>		
Fe g/L	5	1
H_2SO_4 g/L	50	60
NH_3 g/L	2	27

G. Oxidizing Leach Residue Treatment (Fig. 2)

The oxidizing leach C will recover copper (> 95%) and residual iron (~ 80%) leaving residual sulfides, elemental sulfur, silicious residues, and by-product values (mainly precious metals). If copper extraction is less than about 99%, some of the residues need to be recycled to the oxidizing leach C, in order to extend their residence time. But first, it is desirable to separate silicious material and elemental sulfur from the residues.

10 The options chosen for these separations are: flotation for silica rejection (this will also reject oxides formed during roasting that remain unleached) and an undefined sulfur extraction. The bulk of the sulfur would be expected to be filterable on fusion above 119°C. Residual sulfur in the filter cake is probably most easily removed in an aqueous alkali leach (NaOH, NaOH/Na₂S, Ca(OH)₂, or (NH₄)₂S solutions that form polysulfides and thiosulfate). Alternately, a non-
20 aqueous solvent can be used, such as perchloroethylene. In any case, sulfur must be removed quantitatively from any material recycled to the leach, because residual sulfur stifles reactivity in the leach.

Summary of Option II

Option II differs from Option I in that the circulating load of copper is minimized by eliminating sulfur in a roaster, thereby decreasing the copper required to convert remaining sulfur to chalcocite in the reduction leach. Although a dead
30 roast forming copper ferrites is assumed in the flow diagrams, any sulfur eliminating roast is acceptable, including a sulfating roast that produces basic copper sulfate. Any sulfate present in roaster calcines reduces proportionately the requirement

of new sulfuric acid in the circuit that arises from loss of sulfate in the form of jarosite.

The minimum circulating load of copper that can be envisioned is the amount of copper powder needed for the purification circuit. This is difficult to estimate but may be about 25% of production in the hydrogen reduction, or 33% of the copper in the feed. The minimum amount of copper needed in a reduction leach utilizing hydrogen is zero, but all impure copper such as spent purification powder should be returned to the reduction leach. The reduction leach is also an excellent point for feeding scrap copper (powdered or atomized).

Since option II is not entirely hydrometallurgical, but retains a roasting step, it will not be as environmentally acceptable as option I. However, the leaching and hydrogen reduction steps will be much smaller, and this will more than offset the economic penalties incurred by the roasting and acid production steps as well as the optional scavenging acid leach.

Example 1

Fifty grams of copper concentrates (Phoenix mine, Granby Mining Company), 32.9% Fe, 24.3% Cu, 37.8% S, were reacted with one liter of a solution containing 63.5 g/L Cu as copper sulfate at 180°C under 400 psig hydrogen pressure in a stirred 2-liter Parr Autoclave for 2 hours. The final solids assayed 0.017% Fe and 74.5% Cu, while the solution contained 0.57 g/L Cu and 15.04 g/L FeSO_4 . This represents iron extraction of about 99.9%.

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Example 2

21.5 grams of Bethlehem copper concentrates assaying 20% Fe and 32.7% Cu were reacted with 9 grams of copper powder and 50 mls of solution containing 90 g/L Cu as copper sulfate, 20 g/L free H_2SO_4 , and 132 g/L $(NH_4)_2SO_4$ in a small 100 ml shaking autoclave under 100 psi carbon monoxide pressure at $140^\circ C$ for 4 hours. The resulting solids weighed 28.1 grams and contained 0.4% Fe, while the solution filtrate contained 7.2 g/L Cu and 83.0 g/L Fe as sulfate salts. This represents an iron extraction of about 97.4%.

Example 3

237 grams Ruttan copper concentrates assaying 26% Cu, 32% Fe, 3.7% Zn, and 35% S were reacted with 189 grams of -400 mesh copper powder at $140^\circ C$ in 800 mls of solution containing 90 g/L Cu as $CuSO_4$, 20 g/L H_2SO_4 , and 132 g/L ammonium sulfate. Reaction conditions were $1\frac{1}{2}$ hrs. in a two-liter stirred Parr Autoclave at $140^\circ C$ under a nitrogen atmosphere. The resulting solids weighed 413 grams and contained 0.85% Fe, 76.2% Cu, 0.68% Zn, and 18.6% S, while the resulting solution contained 0.26 g/L Cu, 83.7 g/L Fe, 2.77 g/L Zn and 9.6 g/L H_2SO_4 . The iron extraction was 95.1% and the zinc extraction was 44%, while copper removal from solution was 99.7%. The Ruttan Mine is in Manitoba.

Example 4

6.85 g Ruttan concentrates and 5.77 g Ruttan calcines (concentrates roasted at $700^\circ C$ and assaying 36.5% Fe, 28.1% Cu, 2.30% Zn, and 1.2% S) were reacted with 50 mls of solution containing 90 g/L Cu as $CuSO_4$, 20 g/L H_2SO_4 , and 132 g/L $(NH_4)_2SO_4$ at $140^\circ C$ for 1 hour under 400 psig H_2 pressure. The final solution contained 3.3 g/L Cu, 64.1 g/L Fe, 4.73 g/L Zn and 36.5 g/L free H_2SO_4 , while the solid residues assayed

62.6% Cu, 9.2% Fe, 0.47% Zn and 20.2% S. This represents extraction of 74.9% of the iron and 87.3% of the zinc in the concentrate-calcine mixture.

Example 5

6.85 g Ruttan concentrates and 5.77 g Ruttan calcines (as in Example 4) were reacted with 50 mls of solution containing 90 g/L Cu as CuSO_4 and 20 g/L H_2SO_4 (no $(\text{NH}_4)_2\text{SO}_4$) in an otherwise identical experiment to Example 4. The final solution contained 5.6 g/L Cu, 68.2 g/L Fe, 4.90 g/L Zn, and 85.8 g/L free H_2SO_4 . The solids assayed 63.6% Cu, 7.6% Fe, 0.46% Zn and 20.1% S. This represents extraction of 81.5% of the iron and 88.5% of the zinc.

Example 6

237 g Ruttan concentrates analyzing 28.2% Cu, 32.2% Fe, 35.9% S and 2.02% Zn and 189 g copper powder (-230 mesh) were reacted with 830 mls of solution containing 90 g/L Cu, 20 g/L Fe, and 132 g/L $(\text{NH}_4)_2\text{SO}_4$ at 140°C for 2.5 hrs under 150 psig nitrogen. The solids were washed and weighed wet (400.3 g). A 10 g sample of solids lost 11.8% of its weight on drying (calculated dry weight of solids: 353 g). Dry assays on this sample were 77.6% Cu, 15.8% S, and 0.45% Fe. Iron extraction was calculated to be 97.9%.

96 g of these wet solids (containing 11.8% moisture) were leached in 1 L of a synthetic solution representing a composite return acid and analyzing 15.8 g/L Cu (as CuSO_4), 3.3 g/L Fe, 115.5 g/L free H_2SO_4 , and 132 g/L $(\text{NH}_4)_2\text{SO}_4$ under 100 psig oxygen pressure at 100°C for 8 hours. This leach produced a residue of about 16 g dry weight analyzing 15.6% Cu and 0.77% Fe and a leach solution containing 81.8 g/L Cu and 3.7 g/L Fe. The extraction of copper was approximately 96% while 70% of the residual iron was also leached.

Example 7

91.1 g of wet solids from the first part of Example 6 (the reduction leach) (containing 9.2% moisture) were leached in 1 liter of a solution similar in all respects to Example 6 except lacking ammonium sulfate and under the same conditions of time, temperature, and atmosphere. The residue weighed 16.90 g (dry) and analyzed 6.7% Cu and 0.54% Fe. This represents a copper extraction of 98.2% and an iron extraction of 75%. The leach solution assayed about 83 g/L Cu, 3.4 g/L Fe, and 17.5 g/L free H_2SO_4 .

Process Option III Reductive Leaching of Dead-Roasted Copper Concentrates (Figs. 3A and 3B)

This process option III represents a similar reduction leach to that in I and II, but leads to metallic copper powder (mixed with insoluble gangue minerals) rather than Cu_2S , because there is little or no sulfide sulfur in the feed calcine. The option III process would produce a crude high grade metallic copper concentrate in very few steps, and the product powder contains all the precious metals of the original concentrates. (Some minor elements such as Se, Te, Sb, As, and Bi would volatilize in the roast and come out of dust collectors ahead of the sulfuric acid plant.) Further, this product, contaminated only with silicious insoluble minerals, would be suitable for a variety of further treatments, such as:

- (a) Melting and casting into anodes for electrorefining.

- (b) Utilizing as a substitute for hydrogen-produced copper powder in the reductive leach process for concentrates (see Option I).

- (c) Shipping to existing smelters for addition to anode smelting furnaces.

- (d) Additional hydrometallurgical refining steps.

Example 8

Concentrates from the Ruttan Mine (Manitoba, operated by Sherritt Gordon Mines Ltd.) were roasted in a muffle furnace with frequent rabbling, to 800°C, to produce calcines of the following compositions:

Fe 36.5%
Cu 28.1%
Zn 2.3%
S 1.2%

- 10 These calcines were treated on a small scale in a zirconium autoclave, and the results obtained are shown in Table I. Only tests III and IV were performed under reducing conditions.

TABLE I
Leaching Tests with Ruttan Calcines

Test No.	I	II	III	IV
Wt. Calcines	10.84	10.84	10.84	10.84
Solution Volume, mls.	50	50	50	50
Leach Temp., °C	180	180	180	180
Leach Time, hr.	1	1	1	2
H ₂ SO ₄ M.	4.04*	4.04*	1.92*	2.42**
(NH ₄) ₂ SO ₄ M.	0	1.0	1.0	1.0
H ₂ Pressure k pascals	absent	absent	2700	2700
(a) Solution analysis				
Cu g/L	57.3	58.1	5.5	10.5
Fe g/L	29.2	9.4	70.0	70.2
Zn g/L	4.55	4.60	5.02	4.94
(b) Solids analysis				
Wt. g	4.43	7.78 [‡]	3.74	3.32
Fe %	55.8	45.7	12.4	10.2
Cu %	3.8	1.0	67.7	75.2
Zn %	0.78	0.23 [‡]	0.04	0.03
S %	1.68	8.46 [‡]	1.38	1.31
(c) Extraction				
Cu %	94.5	97.5	9.0	17.2
Fe %	36.9	11.9	88.5	91.4
Zn %	91.2	92.3	99.4	99.6

* 0.5M in excess of stoichiometric requirement

** 1.0M in excess of stoichiometric requirement

[‡] Residues contain jarosite, NH₄Fe₃(OH)₆(SO₄)₂

These results indicate that (a) non-reducing conditions lead to an unsatisfactory copper-iron separation, mainly due to too much dissolved iron for further treatment, but also imperfect copper extraction; (b) reducing conditions lead to high iron and zinc extractions, as well as low copper extractions.

It was assumed that incomplete iron extractions in leaches III and IV are due to depletion of free acid and heavy bisulfate buffering in the presence of final FeSO_4 and $(\text{NH}_4)_2\text{SO}_4$ concentrations. For this reason, it may be assumed that a supplementary leach of this material by strong sulfuric acid (suitably in an unpressurized reactor) will complete the extraction of iron, leaving copper powder only in the presence of insoluble gangue minerals and contained precious metals.

A simplified 5-step process leading to iron and sulfur removal from copper concentrates is described (Table II). The equations representing the stoichiometry in each step are shown in this Table II, in which α is the fraction of iron removed in the reduction leach and $(1 - \alpha)$ is the fraction removed in the clean-up strong acid leach. Zinc could be allowed to build-up in circulating leach liquor and removed in a later stage with H_2S (as in the S-C process).

The features of this option III process that are particularly meritorious are:

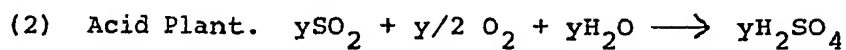
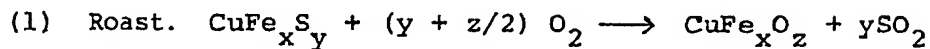
(1) Copper concentrates are upgraded by the selective removal of sulfur, iron, and acid solubles, without significant losses in copper or noble metals.

(2) Sulfur may be removed in a simple dead-roast, or in a partially sulfating roast, both methods by which maximum conversion of product SO_2 to sulfuric acid is possible.

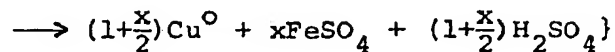
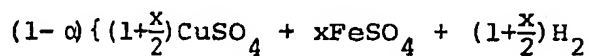
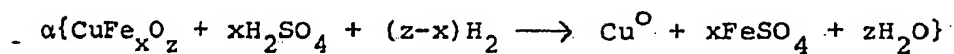
TABLE II

Typical Assays

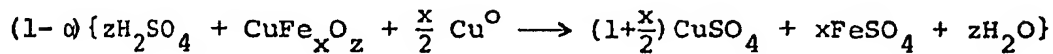
Material	Cu	Fe	Zn	S
(1)	28%	34%	2.0%	36%
(2)	30	36	2.3	1.2
(3)	68	12	.04	1.4
(4)	85	1	.01	1.5
(5)	.02	34	-	13



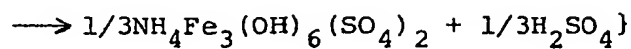
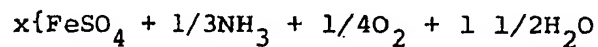
(3) Reduction Leach.



(4) Strong Acid Leach.



(5) Jarosite Precipitation.



(3) Iron is removed as a virtually pure ammonium jarosite, which is convertible, if desired, into a high grade iron ore by calcination.

(4) Zinc is quantitatively removed in such a way that it is recoverable as a high grade zinc sulfide precipitate suitable for treatment in zinc plants.

(5) The final copper concentrate is suitable for refining by many alternative routes, including simple melting into anodes and electrorefining.

10 Some additional experimental tests have been performed on this option III process for converting sulfide copper concentrates to low iron metallic copper concentrates (removal of sulfur by roasting and iron by reduction leaching).

Example 9

 About 3,000 g of Phoenix copper concentrates (24.7% Cu, 31.0% Fe, and 31.0% S) were roasted at 900°C in an electric muffle furnace for six hours. The resulting calcine assayed (on the average) 28.5% Cu, 35.8% Fe, and 1.84% S. 240 g of these calcines were leached using a 2-liter stirred Parr
20 Autoclave in 1 liter of solution containing 151 g/L H_2SO_4 and 132 g/L $(NH_4)_2SO_4$, at 138°C under 400 psig for 3 hours. The resulting solution assayed (without dilution) 71.6 g/L Fe^* , 0.59 g/L Cu, and 7.4 g/L free H_2SO_4 . (*Some $FeSO_4$ crystals seemed to be retained in the solids before washing.) The washed solids from this test (approximately 100 g) contained 63.8% Cu and 6.67% Fe. On the basis of residue analysis, the iron extraction was approximately 87%, while on the basis of solution analysis, the copper extraction was less than 1%.

Example 10

30 Approximately 75 g of the dried product solids from Example 9 were leached in 1 liter of solution containing

151 g/L H_2SO_4 and 132 g/L $(\text{NH}_4)_2\text{SO}_4$ at 100°C for 1 hour. The resulting solution contained 6.11 g/L Fe and 8.74 g/L Cu, while the leach residues assayed 77.7% Cu and 0.22% Fe. This represents an extraction of 97.8% of the remaining iron and about 18.6% of the copper from these residues. The combined total extraction represented by Example 9 and Example 10 was about 99.7% of the iron and slightly less than 20% of the copper. Since the solution of the acid leach of this example is in principle capable of being recycled to a reduction leach such as in Example 9, in which the leached copper is reduced back to metal, the overall copper extraction to the iron leach should not be more than 1%.

Example 11

240 g calcines assaying 28.5% Cu, 35.8% Fe, and 1.84% S were added to the solids of Example 10 and were leached for 3 hours at 140°C in one liter of a solution containing 130 g/L H_2SO_4 , 6.9 g/L Fe, and 8.9 g/L Cu and 132 g/L $(\text{NH}_4)_2\text{SO}_4$ under 400 psig hydrogen pressure. The resulting solution contained 71.0 g/L Fe, 3.7 g/L Cu, and 5 g/L free H_2SO_4 , while 155.4 g solids were produced assaying 5.6% Fe and 58.3% Cu. These results indicate that, not only is 90% of the iron in all the calcines leached, but also, copper is reprecipitated from solution to the solids.

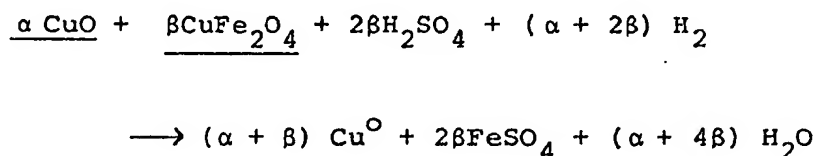
Example 12

240 g calcines assaying 28.5% Cu, 35.8% Fe, and 1.84% S were leached in 1 liter of solution containing 151 g/L H_2SO_4 and 132 g/L $(\text{NH}_4)_2\text{SO}_4$ at 180°C for 1 hour under 400 psig hydrogen pressure. The resulting solution contained 70.3 g/L Fe, 2.67 g/L Cu, and 11 g/L residual H_2SO_4 . The final solids assayed 2.03% Fe and 62.6% Cu. These assays represent an iron extraction

of 97.5% in a single stage. The same solids were leached again with acid at 100°C for 1 hour as in Example 9, and produced solids assaying 84.3% Cu and 0.31% Fe.

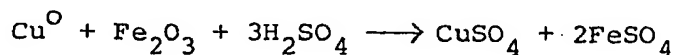
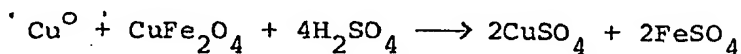
The above results (Examples 9 - 12) indicate that a reduction leach in sulfuric acid at 140 to 180°C under hydrogen pressure will leach iron almost quantitatively from ordinary dead-roasted copper concentrates, leaving a metallized copper residue containing noble elements such as silver and gold, and silicious material present in the original concentrates. Optimum results are presented by strong ferrous sulfate solutions (70 g/L Fe or more) containing little acid (< 20 G/L H₂SO₄) in an ammonium sulfate buffer. This solution is entirely suitable for precipitation of ammonium jarosites as a waste form of iron, the supernatant weak acid being acceptable for recycle to the leach (with make-up strong acid).

The Examples 9 - 12 indicate that the stoichiometry of the reaction approximates the following equation where the copper and iron compounds in calcines



are represented by CuO and CuFe₂O₄.

If a copper product is acceptable with a ratio of Fe/Cu ≤ 0.05, this product can easily be made in a single stage leach at 180°C in 1 hr. However, a 3 hr. leach at 140°C cannot obtain this level of iron extraction, and so a scavenger leach may be necessary for additional iron extraction. The scavenger leach is also a reduction leach, but the reducing agent is contained copper, the stoichiometry being described by the equations:



The scavenger leach is satisfactory at 100°C in an unpressurized vessel and the resulting solution is satisfactory for recycle to the pressure reduction leach. Flow diagrams in Figures 3A and 3B show, respectively, a single-stage reduction leach application and an application with a scavenging leach that leads to very low iron in the metallized product.

Metallized copper residues from the reduction leach can be treated in a number of ways for the recovery of precious metals and refined copper. Among these are:

- (1) Oxygen pressure leaching and electrowinning or hydrogen reduction. The precious metals will then be left in the silicious residues.
- (2) Briquetting, melting (with fluxes), fire refining, casting into anodes, and electrorefining. The melting process must be capable of slagging silicious material and residual iron, as well as eliminating small amounts of residual sulfur. Precious metals would be recovered in anode slimes. This method is conventional.
- (3) Refining by unique hydrometallurgical methods such as leach-filtration-precipitation through a cuprous stabilizing agent (carbon monoxide, acetonitrile, etc.).

CLAIMS:

1. A method of removing iron and recovering copper from minerals, concentrates, tailings or partial calcines comprising these metals at least partly in sulfide form, or from complete calcines thereof in non-sulfide form, comprising:
 - (a) reduction leaching said minerals, concentrates, tailings, partial calcines or complete calcines with an aqueous solution containing sulfuric acid in amounts of the order of about 2 to about 20 g H_2SO_4 /L, at temperatures within about 100°C to about 200°C , under sufficient pressure to avoid loss of water or gas, and while maintaining reducing conditions; said acid concentration and reducing conditions being sufficient to convert substantially all iron present to soluble ferrous salts;
 - (b) in the case of sulfides being leached, providing that a sufficient excess of copper is present to react with all sulfur to form insoluble chalcocite Cu_2S and thereby avoid H_2S emission;
 - (c) separating the leach liquor containing dissolved iron sulphate from solids; and
 - (d) recovering solids containing copper substantially entirely in at least one of the forms Cu_2S and metallic copper.
2. The method of claim 1 wherein the reducing conditions in (a) are maintained by the presence of a selected reducing agent from the group: metallic copper, iron powder, hydrogen-containing reducing gases and organic reducing agents.
3. The method of claim 1 wherein during the reduction leaching, a buffer is present selected from ammonium sulfate, sodium sulfate, magnesium sulfate, and equivalent buffers.

CLAIMS CONT.:

4. The method of claim 2 wherein the reducing agent present is metallic copper powder.
5. The method of claim 4 wherein the copper powder is recycled from reduction leached complete calcines.
6. The method of claim 2 wherein oxides of copper or of both copper and iron are present in the feed material to a substantial extent, and a hydrogen-containing reducing gas is used to provide the reducing conditions.
7. The method of claim 1 comprising the subsequent steps of
 - (e) subjecting recovered solids which contain Cu_2S to a second leach step comprising an oxidizing leach,
 - (f) separating this second leach liquor from unleached solids; and
 - (g) recovering copper from this second leach solution.
8. The method of claim 7 wherein the leach liquor from reduction leach (a) is subjected to jarosite precipitation, the jarosite solids separated to remove iron, and the acid liquor recycled to leaching step (e).
9. The method of claim 7 wherein leach step (e) is comprised of two stages of oxidizing leach, the leach liquor from the initial stage proceeding to copper electrowinning, and the leach liquor from the final stage being used to provide copper for the reduction leach (a).
10. The method of claim 9 wherein the leach liquor from the final stage of an oxidizing leach in (e) is subject to hydrogen reduction to produce a copper powder which is fed as reductant to reduction leach (a).
11. The method of claim 7 wherein prior to the reduction leach (a) the feed material is subjected to a partial

CLAIMS CONT.:

roast step at about 700 - 900°C to remove gases containing sulfur dioxide and the partial calcine fed to reduction leach (a).

12. The method of claim 7 wherein the second leach (e) is an oxidizing leach under oxygen pressure and the final solid residues from this oxidizing leach are treated to recover sulfur and precious metals.

13. The method of claim 11 wherein the gases containing sulfur dioxide are fed to a sulfuric acid plant and resulting acid used in one of the leach steps.

14. The method of claim 7 wherein copper is recovered from said second leach solution in (g) by electrowinning, and the spent acid electrolyte returned to said second leach step (e).

15. The method of claim 7 wherein copper is recovered from the solids containing Cu_2S in a single stage oxidizing pressure leach in step (e), the resulting second leach solution is purified by contacting with copper powder, the purified solution is then treated for copper recovery in step (g) by hydrogen reduction, and part of the product copper powder is used firstly for purification of said second leach solution and secondly for return to the reduction leach (a).

16. The method of claim 1 wherein the feed material initially is dead-roasted at above 700°C to remove sulfur and the resulting calcine then reduction leached, the solid residue being recovered as a metallic copper concentrate.

17. The method of claim 16 wherein a hydrogen-containing reducing gas is reductant during the reduction leach.

CLAIMS CONT.:

18. The method of claim 16 wherein the solid residue is subject to a strong acid leach to scavenge iron and the residue recovered as the metallic copper concentrate.
19. The method of claim 1 wherein the aqueous solution in step (a) contains sulfuric acid in about 10-15 g H_2SO_4 /L.
20. The method of claim 1 wherein the reduction leach is followed by an acid leach to scavenge more iron from the solids.



COPPER HYDROMETALLURGY VIA REDUCTION LEACH

Option I - No Roasting

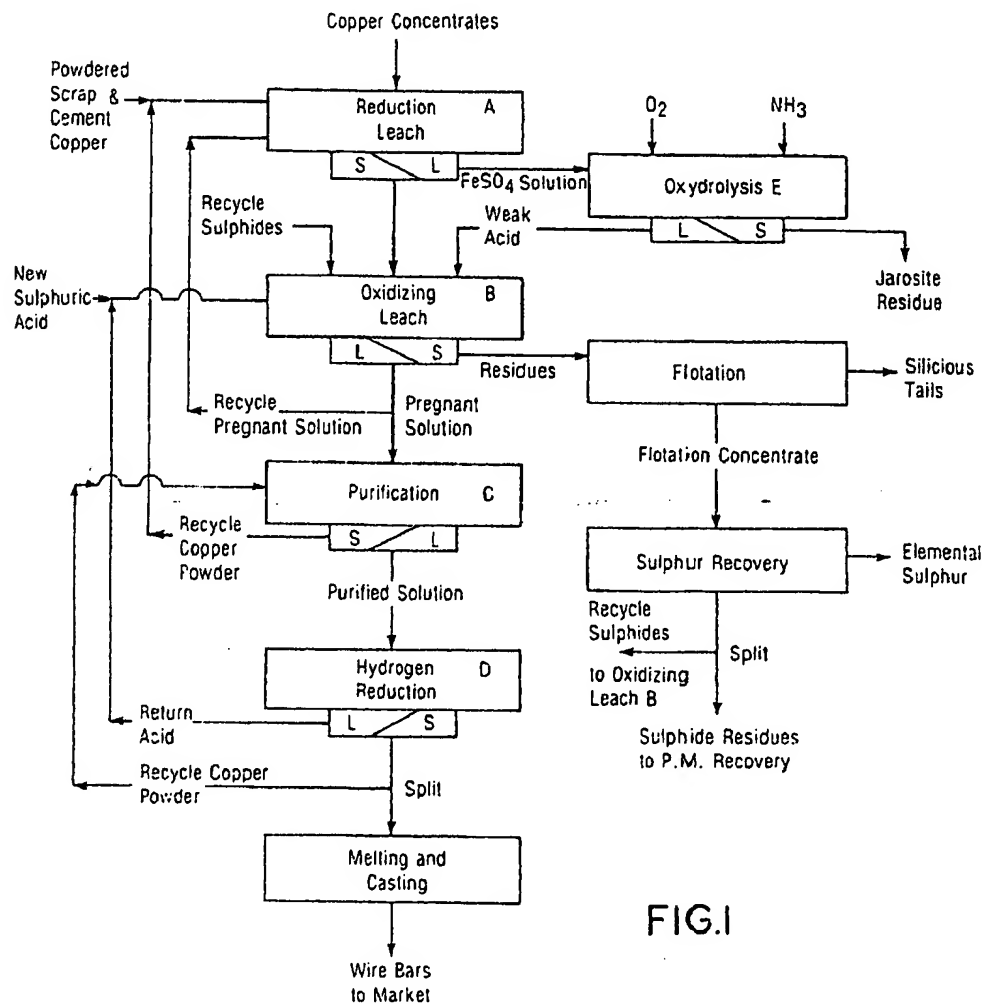


FIG.1

*Don't know
Siegert*

COPPER HYDROMETALLURGY VIA REDUCTION LEACH

Option II - Partial Roast

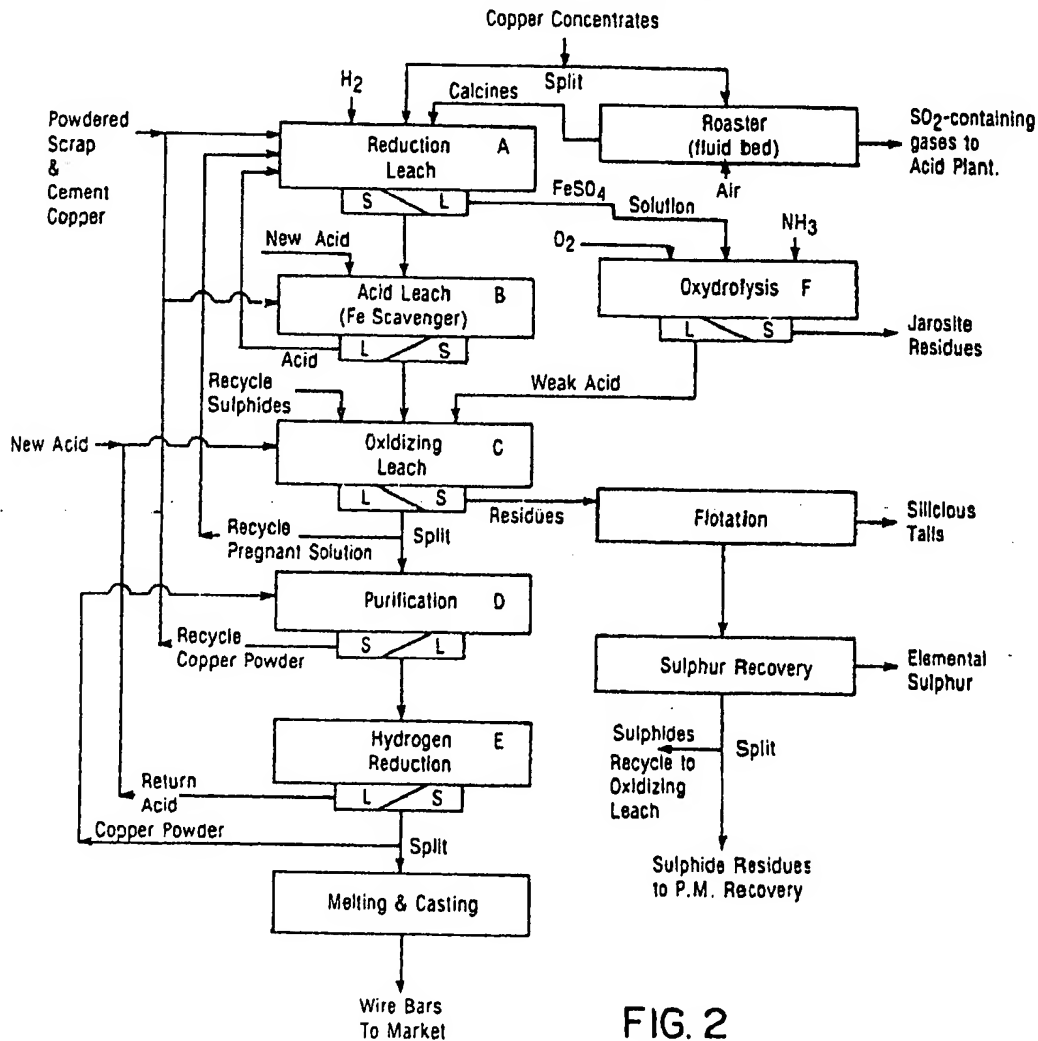


FIG. 2

David A. Thomas
Agent

100% DEAD ROAST OF COPPER CONCENTRATES

Option III

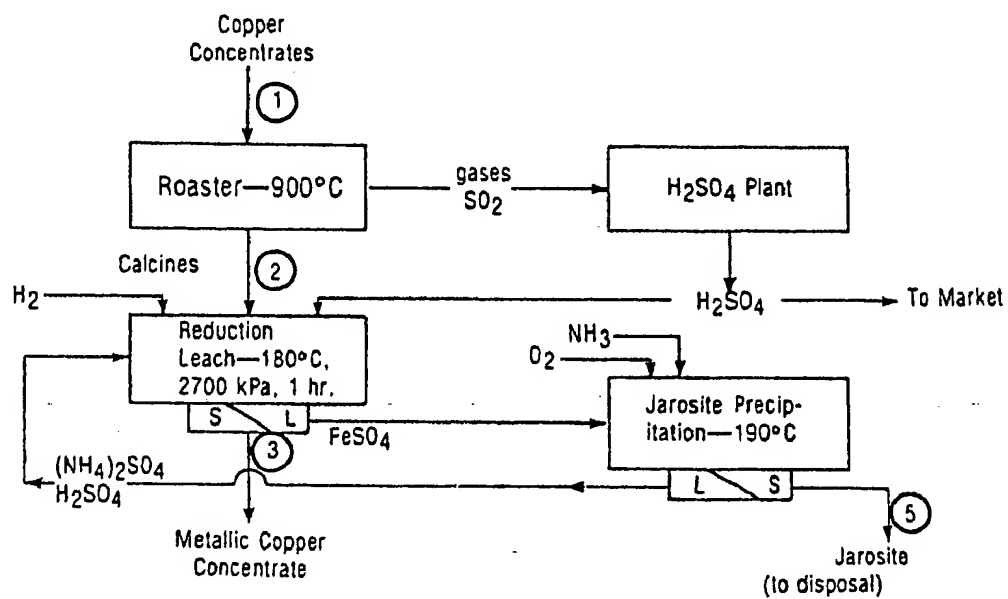


FIG. 3 a

William B. Thomas
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100% DEAD ROAST OF COPPER CONCENTRATES
Option III

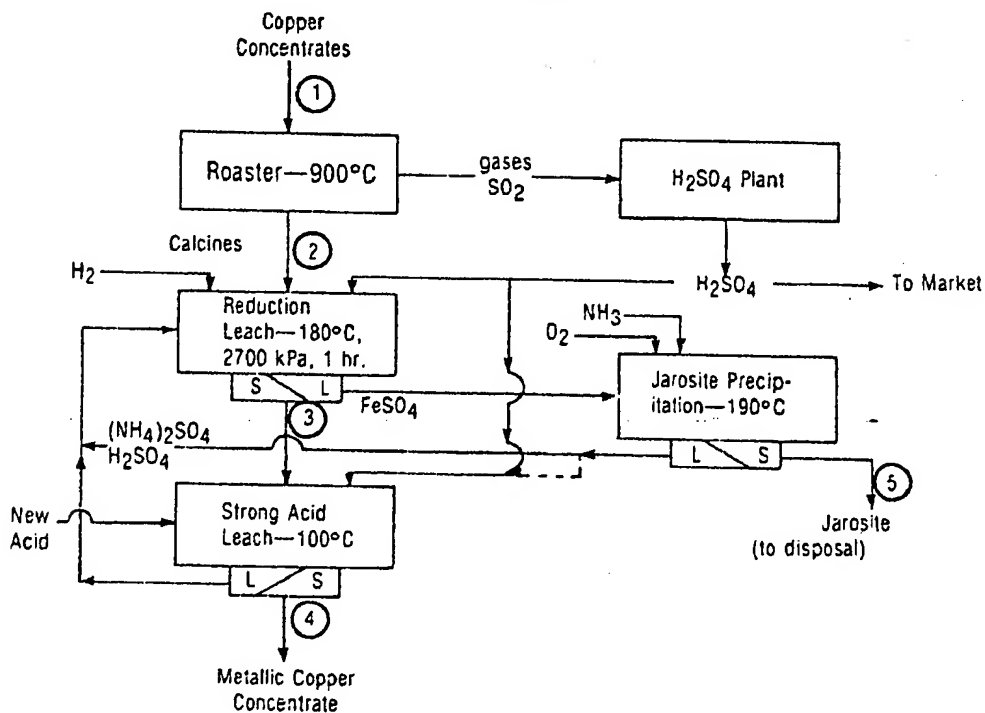


FIG. 3 b

Allen C. [Signature]
Agent